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DAAG29-81-K-0119

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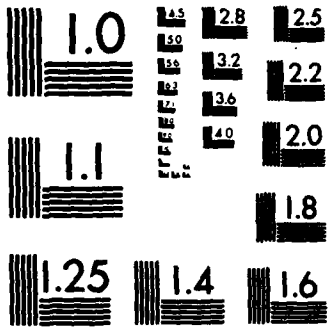

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MICROSTRUCTURE DEVELOPMENT IN POLYMERS

Final Report

Jerold M. Schultz

13 August, 1984

U. S. ARMY RESEARCH OFFICE

Grant Number DAAG 29-81-K-0119

University of Delaware

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: ARO 17795.3-MS	2. GOVT ACCESSION NO.: N/A	3. RECIPIENT'S CATALOG NUMBER: N/A
4. TITLE (and Subtitle): Microstructure Development in Polymers		5. TYPE OF REPORT & PERIOD COVERED: Final 15 Jun 81-14 Jun 84
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): Jerold M. Schultz		8. CONTRACT OR GRANT NUMBER(s): DAAG 29-81-K-0119
9. PERFORMING ORGANIZATION NAME AND ADDRESS: University of Delaware, Newark, DE 19716		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: N/A
11. CONTROLLING OFFICE NAME AND ADDRESS: U. S. Army Research Office, Post Office Box 12211, Research Triangle Park, NC 27709		12. REPORT DATE: 13 August, 1984
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report): Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Polymers	X-ray Scattering
Transformations	Processing
Crystallization	Neutron Scattering

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The development of microstructure in strained and in relaxed polymer systems has been studied. Results for crystallization of Nylon 6.6 and polyester fibers shows a competition between amorphous relaxation and the growth of fibrillar crystals. A transformation theory for stress-assisted transformation in terms of a defective thermal dendrite model has been proposed. Preliminary SANS work on PET has been successful. Quiescent crystallization studies of TMPS crystallization have been made and have resulted in a transformation-front description of reversible crystallization during cooling. Research on the adhesion of

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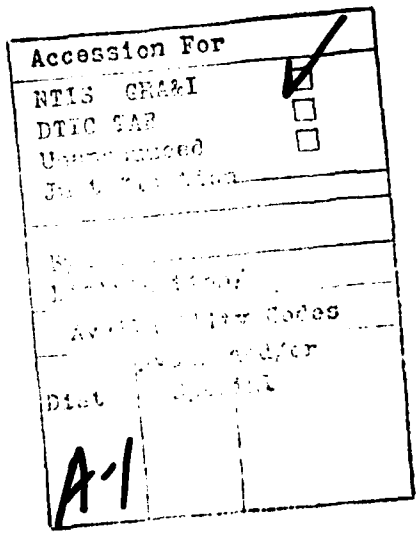
thermal/compression-bonded polypropylene laminates has shown large roles played by relative laminar orientation and prior heat-treatment.



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FINAL REPORT

The area of work pursued with this grant was that of microstructural development in polymers. The research was divided into three program areas: transformations in materials under simultaneous large strain, crystallization from a relaxed melt, and interlaminar bonding in hot-pressed, oriented polypropylene laminates. These areas are treated separately below.

A. Transformations in Strained Systems

The purpose of this research has been to document and characterize as thoroughly as possible the development of crystallinity in highly stretched systems. As a result of the characterization a new theory of stress-assisted crystallization has emerged.

In one portion of the work, isothermal crystallization in oriented fibers has been studied. The course of recrystallization in warm-stretched Nylon 6.6 fibers was studied, using an apparatus developed in the previous grant period by K. M. Gupte[1]. In this previous work, the microstructure was characterized every 30 msec, the time-resolution limit of the apparatus, during isothermal heat-treatment. In a still more thorough study, isothermal transformations in as-spun poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) were characterized, using a redesigned apparatus,[2] capable of a time resolution of 10 msec.

The Nylon 6.6 results showed two stages of transformation.[3] The initial state of these fibrils consisted of dispersed, highly imperfect crystals in an amorphous matrix. In the first stage of transformation (0-60 msec), the crystallites grow and become more perfect. In the second

stage, extending to hundreds of milliseconds, the amorphous material relaxes and the crystals reorient. The elastic modulus drops during this latter stage.

The time-resolved PET and PBT work[3] has also shown a strong competition between melt-relaxation and crystallization. Here, melt-relaxation is ordinarily the first stage and requires very high time resolution for observation. Small-angle x-ray scattering (SAXS) results show a segmented fibrillar morphology for the crystals. Initially imperfect crystals grow more perfect as the transformation progresses.

Based on kinetic and microstructural aspects of stress-assisted transformation, we have proposed a new theory of crystallization under high strain[5]. It is shown that only a rodlike thermal dendrite can disseminate the heat of fusion rapidly enough to produce measured transformation rates. In fact, the crystals must initially be very imperfect, in order to reduce the effective heat of fusion. These concepts are developed quantitatively into a defective dendrite kinetic model.

In yet another portion of this work, small-angle neutron scattering (SANS) specimen preparation methods have been developed for the study of transformations in PET. The goal is to use SANS to follow single chain dimensions during deformation and subsequent heat-treatment. In order to perform SANS work, it was first necessary to produce void- and segregation-free specimens[6]. In a second preliminary work, the temperature and time limits within which one can operate without encountering transesterification has been documented and SANS has been shown to be an effective gauge of such exchange reactions[7]. Preliminary

results on cold-stretched PET are promising.

Finally, concepts of stress-assisted crystallization were used in assembling a review of the microstructure developed during the injection molding of semicrystalline thermoplastics.[8]

B. Crystallization of Relaxed Melts

With Prof. J. H. Magill (University of Pittsburgh), we have completed in-situ SAXS measurements during the crystallization and subsequent cooling of poly(tetramethyl-p-siphenylene-siloxane) (TMPS) fractions. These crystallization results are still being analyzed. A large and reversible decrease in long period during cooling has led to a new interpretation of how crystallinity develops upon cooling. The long period results are consistent only with a model in which a morphological front moves through the material.

C. Adhesion in Polypropylene Laminates

The problem of adhering oriented plies of a polypropylene laminate without significant loss in orientation and modulus has been studied[9]. Results show strong effects of temperature and pressure, as expected, but also of the relative orientation between plies and of prior annealing. This work is not yet complete, but is pointing toward a model in which crystals in one lamina grow into amorphous zones in an adjacent lamina.

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1. K. M. Gupte, Heike Motz, and J. M. Schultz, J. Polymer Sci., Polym. Phys. Ed., 21, 1927 (1983).

2. Perla N. Peszkin and J. M. Schultz, submitted to J. Appl. Polymer Sci..

3. J. Elad and J. M. Schultz, J. Polymer Sci., Polym. Phys. Ed., 22, 781 (1984).

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List of Publications

A. Published

1. S. S. Katti and J. M. Schultz, "Injection Molding: Microstructure and Properties -- A Review," Polymer Engineering and Science, 22, 1001-1018 (1982).
2. K. M. Gupte, Heike Motz, and J. M. Schultz, "Microstructural Rearrangement During the Heat-Treatment of Melt-Drawn Poly(Ethylene Terephthalate) Fibers," Journal of Polymer Science, Polymer Physics Edition, 21, 1927-1953 (1983).
3. J. Elad and J. M. Schultz, "Microstructural Rearrangement During the Heat-Treatment of Drawn Nylon 66 Fiber," Journal of Polymer Science, Polymer Physics Edition, 22, 781-792 (1984).
4. W. A. Tiller and J. M. Schultz, "Crystallization of Polymers Under High Tension: A Dendrite Model," Journal of Polymer Science, Polymer Physics Edition, 22, 143-161 (1984).

B. In Press

1. K. P. McAlea, J. M. Schultz, K. H. Gardner and G. D. Wignall, "Molecular Dimensions in Polyethylene Terephthalate by Small-Angle Neutron Scattering," Macromolecules, in press.

C. Submitted

1. Perla N. Peszkin and J. M. Schultz, "Kinetics of Fiber Heat-Treatment I: Experimental Apparatus," submitted to Journal of Applied Polymer Science.

List of Scientific Personnel

1. Principal Investigator

   Dr. Jerold M. Schultz

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   Dr. George D. Wignall, Oak Ridge National Laboratory

   Dr. William A. Tiller, Stanford University

   Dr. KennCorwin Gardner, E. I. du Pont de Nemours & Co.

   Dr. Joseph H. Magill, University of Pittsburgh

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   Ms. Perla N. Peszkin (will receive Ph.D. in September 1984, under ARO sponsorship)

   Ms. I-Hwa Lee (currently pursuing M.Ch.E. degree)

   Mr. Kevin McAlea (currently pursuing M.Ch.E. degree)

4. Undergraduate Students

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   Mr. Daniel Leeser

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